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(54) Title: FOODS COMPRISING A GEL COMPOSITION AND PROCESS OF MANUFACTURE

Foods comprising a gel composition and process of manufacture

Background of the Invention

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The present invention relates to gels and their use in foods.

In particular the invention relates to gels made with polyanionic gelling hydrocolloids, because such give pleasing textures with visual clarity, wobble, strength, minimal adhesiveness and good flavor release and mouthfeel.

Additionally, such gels give stabilization to foams, emulsions and suspensions etc.

Gels may be prepared by a variety of methods and from a variety of materials. However, in order for controlled dosing and shaping, such techniques normally require an initial preparation of a fluid hydrocolloid solution called a sol that has to be heated, held hot and hot-filled into molds.

Typically, this sol will degrade if held hot for any significant period of time. Such degradation leads to losses of gel strength in the ultimate gel and to the introduction of increasing degrees of adverse adhesiveness in the final product.

Yet, if allowed to cool, such a sol will set, with adverse effects both to production handling and to finished product quality.

For the purposes of many types of food preparation, the components are first heat treated in some way such as cooked, pasteurized etc. and then held for a period of time until utilized in either a shaping/forming process or similar. In such a process, the heat serves many purposes including for microbiological benefit, and additionally converts gelling materials into their liquid state (known as a sol) a form in which they are more easily processed.

In a production process, even with all due diligence paid to forward planning, it is always possible that heat-treated, part-processed material may need to be kept for periods (for example in excess of 24 h). It is for proper microbiological and hygiene reasons, to avoid spoilage, that such storage is more typically under cold conditions. However, under such conditions, many gelling materials (although

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originally in sol state) will unfortunately prematurely set (gel) in the process before becoming part of the final product.

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If premature gelation has occurred as a result of cooling, the temperature has to be elevated much higher than the setting temperature in order to reconvert the gel, back into a sol. In many cases the difference between melting and setting temperatures is so large as to render this impractical or impossible.

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For more limited periods, such part-processed materials (as sols) may be kept hot (for example for 1-8 h) to prevent premature gelation from occurring.

Unfortunately, under such conditions, thermal degradation of the product invariably results to a greater or lesser degree. At worst, the final product may fail to gel and can assume an adhesive, viscous aspect. At best, there will still be some variability in gel strength in accord with the time and temperature history of the keeping.

Thus one objective of the invention is to be able to produce in a conventional process, a product with novel eating qualities of a gel that has not undergone hotstoring and hot-filling. In terms of process efficiency and possible damages to equipment, particularly welded parts, it is desirable to limit or even avoid very hot-filling, e.g. at temperatures in excess of about 50 °C. Holding the sol at cold post pasteurization conditions permits certain simple energy savings. This is because the pasteurizer exit heat can then be withdrawn from the product in a regeneration heat exchanger so warming up the pasteurizer product feed.

The invention also includes combinations of polyanionic gelling hydrocolloids, preferably e.g. carrageenan plus pectin, because the rheological properties of binary hydrocolloid mixtures are related to the microstructure.

Other polyanionic gelling hydrocolloids would include most marine or seaweed extracts, e.g. agar, alginate, furcelleran etc., and certain of the microbial polysaccharides, e.g. gellan, xanthan, succinoglycan etc.. Some other hydrocolloids such as carboxymethylcellulose (CMC) could be captured under the term polyanionic hydrocolloids, but these would not be captured under the name polyanionic gelling hydrocolloids and are therefore not contemplated in the invention.

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Other hydrocolloids may be beneficially included in the formulations.

Neutral hydrocolloids that do not typically gel on their own are included in the worked examples. This because a synergism is observed for mixtures of locust bean gum (LBG) and polyanionic hydrocolloids, which shows a strong dependence upon the ionic environment.

Further LBG is not observed to increase the "solidity" or G prime, under ionic conditions of excess sodium cations. In fact in such conditions, LBG hinders natural self-association of the polyanionic gelling hydrocolloids by influencing the supermolecular structure.

Similar neutral hydrocolloids would include all the uncharged seed gums, particularly the galactomannans, certain extrudate gums, and even some root cell polysaccharides such as Konjac.

Background Art

JP 2000 004793 relates to an iced dessert with a jelly-like solid item coated with ice cream. This product is jelly-like, not a true gel and is produced by insoluble dietary fiber such as sweet potato fiber.

JP1118789 relates to a frozen dessert containing sugar alcohols and curdlan.

Curdlan is not a polyanionic hydrocolloid. Curdlan is a non-ionic polysaccharide derived from the microbe called A. faecalis and has a linear beta 1-3 glucose backbone. Curdlan is not an approved food material in USA or Europe and the conditions under which it forms its gel are not those used in many of the processes of the food industry. Curdlan is insoluble in cold water and undergoes hydration and subsequent gelation upon heating at above 80 °C.

JP 2000 50802 relates to the formation of a ring design using two fluid ingredients of different color and does not relate to a gel, or to a method of making a gel.

JP 1999 346659 relates to a swirl design food based upon molding and nozzle devices. It does not relate to a gel, or to a method of making a gel.

JP 1973 20313 relates to the use of alginates as ingredients within shape retaining ice cream. After thawing, the alginates absorb the water that is released from the melting ice. This does not relate to a separate gel, or to a method of making a separate gel, although it is acknowledged that the thawed ice cream does itself have some gel character.

DDR 1978 0152 582 relates to the process of utilizing enzymes to create hydrolysed maize starch that in a heated aqueous suspension forms a dextrinaceous mass (15 DE, dextrose equivalent) that gels upon cooling. This does not relate to a polyanionic gel, or to a method of making a polyanionic gel. The process requires a temperature of 95-100 °C in order to inactivate the enzyme. Such temperatures have been found to be antagonistic to polyanionic hydrocolloids in the absence of a gel inhibitor.

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US 4 985 263 discloses a method for coating a frozen confection product containing calcium ions by dipping the frozen confection into a flowable aqueous medium containing an alcali metal alginate to form a coating thereon and spraying the coated product with an aqueous solution of a calcium salt. It is believed that the calcium in the frozen confection reacts with the alcali metal alginate in the flowable aqueous medium to form a gel on the surface of the frozen confection and that the calcium salt in the spray reacts with the alcali metal alginate in the coating to form a gel on the outside surface of the frozen confection.

25 <u>Summary of the invention</u>

The products contemplated by the invention comprise in particular or combinations of other food materials with gels that are:

Jelly products of highly consistent and controllable gel strength - in excess of 25 g by stated method (see below).

Jelly products of relatively low adhesiveness - less than 5 g.s by stated method (see below).

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Products that are consistent in gel character, being neither too soft nor too hard.

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Products that have controlled adhesiveness in the gel aspect.

Products that may be made in a typical factory using existing equipment assets.

Unique products that could not be made before.

The invention further contemplates a method that can be utilized to prepare such items without inherent changes in ultimate gel nature (or loss of gel character) happening. Such method involving the use of a gel inhibition mechanism during the preparation and storage of the sol, followed by a neutralization of said gel inhibition mechanism immediately prior to the dosing, forming, shaping or other process mechanisms.

- There are 4 main problems that are solved with in this current invention. These problems are as follows:
 - 1. The hydrocolloid degradation that results from hot storage leads to weakening of the products. As the sol's time duration during hot storage is not precise, this results in products that have variable textural properties. Such variable characteristics lead to products that are inconsistent in process handling characteristics. This leads to excessive product rejection and also to line blockages. Very importantly, it also leads to products that are inconsistent for the consumer. Such inconsistencies may present themselves to a varying degree, product by product and batch by batch. Softness of texture will lead to shape losses, and these may occur rapidly during any temperature change that occurs to the product during the time period of preparation and consumption.
 - These variations cannot be overcome by simply increasing the hydrocolloid concentration. Alternatively, hardness of texture (a result of using excess hydrocolloid to overcome thermal degradation) will lead to losses of wobble, poor flavor release and unpleasant rubberiness. It is essential to achieve a gel character that is of consistent hardness.
- 2. Thermal degradation leads to a greater proportion of products that completely fail to gel. Products that do not gel fail to deliver the desired textural

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characteristics to the consumer. They are more susceptibly to falling apart and may readily disengage from the other aspects of the product. In frozen products, they melt leading to excess dripping. They fail to control ice crystal growth leading to products that suffer heat shock damage in distribution systems. They fail to control flavor release leading to excessive and unbalanced initial impact, followed by flavor fade leading to the presence of an unflavored mass in the mouth.

- 3. Thermal degradation of hydrocolloid sols leads to the creation of adhesiveness. Such stickiness or gumminess renders such products difficult to handle in production in operations such as de-molding, lifting off conveyor belts, during wrapping operations etc. From the product point of view, products become difficult to unwrap, and stick to the teeth during eating. Excessive thermal breakdown of sols can even lead to sliminess as well as adhesiveness.
- 4. The forth issue involves colder storage of the sol. Cold storage of sols prior to the shaping and other process leads initially to excess viscosities developing. This slows down material transfer operations by increasing back-pressure, sometimes leading to seal failure. Also it leads to issues with starvation of the 20 feed sections of pumps. The initiation of premature gelling leads to the formation of skins on top of stored sols; these become rings of debris on vessel walls. This results in material losses and, when particles break off, it leads to partial blockages of screens etc. Rather quickly, full premature gelation results, leading to the requirement to dig out process vessels, dismantle pipes and pumps etc. Gelation that occurs prior to product shaping, pre-gelation, will also lead to the presence of shear-damaged gels. Such damaged gels will not re-heal and will result in a consumer perception of slush rather than a gel .

Detailed Description of the Preferred Embodiments

Preferred products comprise simple single gelling hydrocolloid jellies that may for example be formed by molding, layering, rope formation, enrobing, dipping, lamination, co-extrusion, or any of hosts of other shaping possibilities.

The gels may themselves be combinations of hydrocolloids exhibiting synergistic benefits or having unique textural characteristics. Similarly, two or more phase "gel in gel" emulsions may be prepared.

The gels may be part components of two phase or multi-phase combination products. Other phases may include other gels, fluid masses, gases, and solids such as lipid components or inclusions or others.

Examples

The invention is further illustrated by reference to the following Examples describing in detail the methods of the present invention. The examples are representative and should not be construed to limit the scope of the invention in any way. In the following Examples, parts and percentages are by weight unless stated otherwise. In the Examples, gel strength and adhesiveness were determined as indicated below.

Gel Strength/Adhesiveness Measurements

Gel properties were determined using a TAXT/2 texture analyzer on prior frozen samples tempered 24 h at - 16 °C and allowed to thaw under ambient conditions.

Testing was conducted when the surface temperature of the samples was at 25 °C by infrared thermometer.

A TA-18 probe, which is a half-inch diameter stainless steel ball, was used in texture profile analysis mode. The probe is attached to a bi-directional load cell.

The probe was programmed to penetrate the sample to a depth of 1 mm. A speed of 2 mm/s on the "bite" was utilized.

The results were represented in a force time curve.

Hardness is represented as the maximum force in grams during penetration and this point occurred at the maximum penetration distance.

Adhesiveness is represented as the negative area of the force-time curve (g.s) during the ascent of the probe. In other words it is the pull on the probe as it lifts off the sample.

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Example 1: Carrageenan System

a) A sol was prepared from the ingredients indicated in Table 1 below by using the method of preparation indicated below.

Table 1

Ingredient	Parts
Water	61.76
Sucrose	15.00
Corn Syrup, 36 DE, 80% solids	20.00
Carrageenan (kappa)	0.35
Locust bean gum	0.20
Trisodium phosphate	0.20

10 DE: Dextrose equivalent

b) A gel was prepared from the sol formula with additional ingredients as indicated in Table 2 below by using the method of preparation indicated below.

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Table 2

Ingredient	Parts
Sol	97.51
Citric acid solution, 50% solids	1.10
Potassium chloride solution, 10% solids	1.00
Flavor	0.20
Color solution	0.19

c) Method of preparation

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1. The water was heated to 60 °C and agitated at high shear (4,000 rpm by Silverson dispersator or equivalent) and the trisodium phosphate incorporated.

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- 2. The hydrocolloid (carrageenan) was added in a slow stream (to avoid clumps) to the side wall of the vortex. Agitation was maintained until solution was confirmed (lack of visible solid particles adhering to an inserted rod).
- 3. The sucrose and corn syrup were then incorporated.
- 5 4. The sol was then pasteurized at 85 °C on an HTST (high temperature short time) plant.
 - 5. The sol was cooled down to 4 °C and stored in tanks under slow agitation.
 - 6. Within 10 min. of the product forming/shaping operation and preferably immediately prior to it, the sol was heated up to 50 °C and the remaining ingredients for the gel were incorporated by an in-line mixer or equivalent equipment.

Mixing time, in general, depends upon the mixer speed and the product viscosity. Mixing time should be minimized to that required for obtaining uniformity in the product. This time may be established by observing the distribution of the color added to the sol during the operation. Excess mixing times, such as might result from too slow stirring, should be avoided, as in such a case shear damage to a forming gel might result.

- 7. The sol was shaped as desired, which may be in combination with other materials, it was cooled to set, frozen, wrapped and kept in cold storage until sale.
- In this Example, the product's gel was found to have a hardness of 57 g and an adhesiveness of 0.1 g.s.

Example 2: Kappa Carrageenan System

Product was prepared as in Example 1 except that the sol's holding time at 4 °C was varied to establish the effect upon the final gel properties. The results are indicated in Table 3 below.

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Table 3

Time of Sol at 4 °C (h)	Gel Strength of final Product (g)
0	57.2
24	56.8
48	56.7
72	56.8

This was supported by no observable change in the product's adhesiveness value which maintained 0.1 g.s.

This Example demonstrates that holding the sol for extended periods of time does not adversely influence the final gel properties. Similarly, it demonstrates that the product's characteristics were consistently reproduced.

Example 3: Kappa Carrageenan/Pectin System

A sol was prepared from the ingredients indicated in Table 4 below by using the method of preparation indicated in Example 1. A gel was then prepared as in Example 1.

Table 4

Ingredient	Parts
Water	61.41
Sucrose	15.00
Corn Syrup, 36 DE, 80% solids	20.00
Carrageenan (kappa)	0.20
Locust bean gum	0.20
Pectin, 35DM	0.50
Trisodium phosphate	0.20

20 DM: Degree of methoxylation

This Example is illustrative of the use of multiple gelling hydrocolloids in combination.

Example 4: Kappa Carrageenan/Pectin System

Product was prepared as in Example 3 except that the sol's holding time at 4 °C was varied to establish the effect upon the final gel properties. The results are indicated in Table 5 below.

Table 5

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Time of Sol at 4 °C (h)	Gel Strength of final Product (g)
0	43.8
24	43.8
48	46.8
72	43.3

This was supported by no observable change in the product's adhesiveness value which maintained 0.2 g.s.

This Example demonstrates that holding the sol for extended periods of time does not adversely influence the final gel properties. Similarly, it demonstrates that the product's characteristics were consistently reproduced.

Comparative Examples

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Comparative Example 1: Without the gel controller/inhibitor

Product was prepared using the recipe of Example 1, except without the presence of the trisodium phosphate.

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The sol converted to a gel upon cooling. Gelation started to occur at a temperature of 38-40 °C.

This Example confirmed the role of the gel controller/inhibitor.

Comparative Example 2: Holding the sol at elevated temperatures

Product was prepared as in comparative Example 1, except that the sol was held liquid by maintaining at a temperature of 50 °C.

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The sol's holding time at 50 °C was varied to establish the effect upon the final gel properties. The results of gel strength and adhesiveness are indicated in Tables 6 and 7 below.

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Table 6

Time of Sol at 50 °C (h)	Gel Strength of final Product (g)
0	56.3
1	43.8
5	21,.2
10	6.3
15	Liquid

Table 7

Time of Sol at 50 °C (h)	Adhesiveness of Final Product (g.s)
0	0.1
1	1.8
5	9.8
10	15.6
15	Liquid

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This Example confirms that holding the sol at elevated temperature results in changed characteristics to the final gel formed, according to the time at the elevated temperature.

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Comparative Example 3: Holding the sol at elevated temperatures and increasing the level of anionic hydrocolloid (attempting to compensate for a degree of thermal degradation).

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- Product was prepared as in comparative Example 1, except that the carrageenan in the sol was increased to 0.6% (the increase of 0.25 parts of carrageenan was compensated by reducing the water in the recipe by the same 0.25 parts). Owing to high viscosity constraints, this sol had to be held at 60 °C.
- With product produced from sol that had been held for 2 h at this temperature, the gel strength had already fallen to only 15% of that of product made from freshly prepared sol. Product produced from sol that had been held for 16 hours at this temperature failed to gel and remained as a sticky liquid.

15 Example 5: Ice cream bar coated with gel

A sol was prepared as in Example 1 and stored in a stirred tank at 4-10° C. Just before use, the sol was heated to about 50° C in a heat exchanger and the necessary quantity of a solution containing color, flavor, acid and setting salt as in Example 1 was dosed in the line and mixed with the sol by a static mixer and the resulting mixture stored in a stirred tempering tank at 50° C, pending use for gel coating. The tempering tank was connected to a gel coating tank maintained at 50° C through an inlet pipe and the overflow was returned to the tempering tank through a heated outlet pipe.

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A stick ice cream bar with 100 % overrun was produced by extrusion and it form fixed in a freezing tunnel. It was then surface-cooled in a nitrogen bath for 2-5 s, its surface temperature being - 25° C.

The surface-cooled bar was then dipped into the gel coating tank during about 50 s and then hardened 10-20 s in liquid nitrogen, flow-packed and stored at - 30° C.

Example 6: Water ice shell stick bar with gel center

A sol was prepared as in Example 1 and stored in a stirred tank at 4-10° C. Just before use, the sol was heated to about 50° C in a heat exchanger and the

necessary quantity of a solution containing color, flavor, acid and setting salt as in Example 1 was dosed in the line and mixed with the sol by a static mixer and the resulting mixture led to a heated gel dosing unit warmed at 50° C for immediate use for filling at 40-50° C.

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Using a mold line, provided successively with a standard water ice hopper, a suction device and the heated gel dosing unit, molds travelling through a refrigerated brine bath were filled with water ice and, when a frozen layer of about 2 mm thickness was achieved on the side wall of the molds, the liquid contents from the centers of the molds were sucked out. The empty spaces in the molds were then filled with the heated gel in order to produce a shell and core split. The products were quiescently frozen, sticks were inserted, the stick bars demolded by surface-heating, surface-hardened, wrapped and stored at - 30° C.

15 Example 7: Twisted composite water ice stick bar with gel

A composite water ice and gel stick bar was produced as in Example 6 from colored water ice and gel. In so doing a mold in the mold two steps molding process was used with a mold for the core of helicoidal shape for producing the core in the first step and an external mold of frustoconical shape for the gel. The resulting stick bars were in the shape of a contrasted colored double helix.

Using the double mold line, provided successively with a standard water ice hopper and the heated gel dosing unit, a first series of helical molds for the core and a second series of frustoconical molds for the complement were travelling through brine baths. After filling the first series of molds with water ice, the cores were quiescently frozen, stick were inserted, the sticked centers were demolded by surface-heating of the first molds and the cores were placed into the second series of molds which were partly filled with heated gel. In doing so, the liquid gel filled the empty spaces of the second molds and the whole was quiescently frozen. After demolding by heating the surface of the second molds, the products were surface-hardened, wrapped and stored at - 30° C.

Example 8: Blended composite water ice stick bar with gel

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A sol was prepared as in Example 1 and stored in a stirred tank at 4-10° C.

A colored water ice mix was separately mixed in a stirred tank at 4-10° C with the necessary quantity of a setting salt.

- The sol and the water ice with setting salt of contrasted colors were dosed from positive displacement hoppers in the line and blended by a static mixer and the resulting mixture led to a cold gel dosing unit for filling molds travelling through a refrigerated brine bath. The proportions of gel/water ice mix were 50/50 to 70/30.
- Sticks were inserted, the products quiescently frozen, demolded by heating the surface of the molds, surface-hardened, wrapped and stored at 30° C.
- The composite stick bars so produced had a new contrasting aspect and a new contrasted texture of ice and gel.

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Claims

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1. A food product comprising as ingredients an anionic gelling hydrocolloid and a gelation controller or inhibitor, and which either comprises a gel having a hardness of between 25 - 150 g and an adhesiveness of less than 5 g.s.

- 2. A product according to claim 1, with a preferred hardness of between 35 100 g and an adhesiveness of less than 3 g.s.
- 3. A method for preparing a gel which comprises making a liquid sol containing an anionic gelling hydrocolloid together with a gel controller or inhibitor, followed by a neutralization of the gel controller or inhibitor's influence immediately before product shaping, forming and packaging.
- 4. A method according to claim 3, in which the preferred gel controller or inhibitor is trisodium phosphate.
 - 5. A method according to claim 3, in which the gel is hot filled into molds and the molds are quiescently frozen.
 - 6. A composite food product comprising multiple components, wherein the gel product of claim 1 is present as one of the components of the product.
 - 7. A composite food product according to claim 6, which is a frozen confection.
 - 8. A composite food product according to claim 6 or 7, wherein a first component is a shell or a coating and a second component is a core.
- 9. A composite food product according to claim 8, wherein a first component is a30 gel coating.
 - 10. A composite food product according to claim 8, wherein the core is a gel.
- 11. A composite food product according to any one of claims 6 to 10 in the form of a stick bar.

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- 12. A method for preparing a composite food product, which comprises making two mixes, one with an anionic gelling hydrocolloid and a gelation controller or inhibitor, the other with a water ice and a setting salt, cold blending the two mixes, filling the blended mixes into molds, quiescently freezing, inserting sticks, demolding and packaging.
- 13. A method for preparing a composite food product, which comprises filling molds with a water ice mix, forming a frozen layer on the side wall of the molds, sucking out the liquid contents from the centers of the molds and filling the empty spaces in the molds with heated gel which is formed from a sol containing an anionic gelling hydrocolloid and a gelation controller or inhibitor and is converted into a gel by neutralization of the gel controller or inhibitor, in order to produce a shell and core split, quiescently freezing, inserting sticks, demolding and packaging the stick bars.
- 14. A method for preparing a composite food product, which comprises forming a frozen core of ice confectionery and coating it with heated gel which is formed from a sol containing an anionic gelling hydrocolloid and a gelation controller or inhibitor and is converted into a gel by neutralization of the gel controller or inhibitor, in order to produce a gel-coated core and then hardening and flow-packaging it.

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A23G9/02 A23L A23L1/0532 A23L1/054 A23L1/0524 A23G9/04 A23G9/24 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) IPC 7 A23G A23L Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) PAJ, WPI Data, EPO-Internal C. DOCUMENTS CONSIDERED TO BE RELEVANT Category Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. X US 2 059 541 A (THOMPSON DONALD R ET AL) 1-3,5,6,3 November 1936 (1936-11-03) 11,12 page 2, column 1, line 26 -column 2, line 41; claims 1-5 page 2, column 2, line 63 -page 3, column 1, line 10 page 3, column 2, line 24 - line 42 page 4, column 1, line 8 - line 33 page 1, column 2, line 6 - line 53 Υ US 3 367 784 A (HOOS JOSEPH W ET AL) 6 February 1968 (1968-02-06) column 4, line 3 - line 38; examples Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the *A* document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another clietion or other special reason (as specified) document of parlicular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled "O" document referring to an oral disclosure, use, exhibition or document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the International search report 6 June 2002 01/08/2002 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3018 Guyon, R

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